

Evaluation of Oils from the Manufacture of Carburetted Water Gas by Their Available Hydrogen Content

EXTRACTED FROM A DISSERTATION SUBMITTED BY PETER J. MERKUS
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The manufacture of carburetted water gas has reached a high state of technical development and when a new carburetting oil is to be introduced, modifications of plant operation are tested until the most desirable method of operation has been found. When operating conditions have been adjusted until the best results are obtained, the carburetting values as found in plant practice may be considered as due mainly to the composition and chemical nature of the oil used and only in a minor degree to defects in its treatment in the water gas set. It has only been since the introduction of the modern mechanically operated machines, that the water gas set has reached a position where it may be considered as a scientific instrument of considerable precision and so it has only been within the last few years that it has been feasible to attempt to correlate the chemical composition of the oil with its carburetting value as revealed in practice. It is also only within a relatively few years that gas oils of widely varying chemical compositions including cracked residuums and asphaltic base oils have been successfully used as gas oils.

The earlier investigators of the carburetting value of gas oils met with little success in correlating chemical composition, specific gravity, distillation curves, and laboratory cracking tests with the results obtained in the plant. Their lack of success was due in part to the uneven results of plant operation, and in part to the crudity of the laboratory cracking units. These latter have now been improved to the point where conditions are under close control and reproducible results are readily obtained.

Griffith¹ proposed a method for analysis by which the constituents of a gas oil could be separated with approximate accuracy into paraffines, naphthenes, aromatics, and unsaturates. Mighill² proposed a method of analysis leading to a sim-

ilar classification. He proposed the following table of carburetting efficiencies:

Paraffines	80%
Naphthenes	70
Aromatics	50
Unsaturates	25

Wing³ showed that these analytical methods gave erratic results, and cited one oil which when tested by three skillful analysts showed such widely different figures as 5.4 and 60.3% of naphthenes, and 23.5 and 75.4 of paraffines.

Holmes⁴ proposed a relation which involved specific gravity, dispersion of light and the average boiling point of the oil, and showed that there was considerable correlation between his calculated results and those obtained in a laboratory cracking furnace.

The variation in the chemical composition of the fractions of various crude petroleum has been excellently summarized by Frolich⁵ in the following statement:

"The types of hydrocarbons present in petroleum vary with the origin of the crude oil, but in all cases the lower fractions consist of paraffin hydrocarbons ranging from methane upward. The intermediate cuts are partly paraffins and partly single-ring naphthenes, while the heavier components consist largely of single and condensed rings with paraffinic side chains of varying length. Although simple paraffin hydrocarbons of high molecular weight are found in considerable amounts particularly in the so-called paraffin base crudes, Mabery's work has shown beyond doubt that the greater portion of the paraffinic constituents exist as radicals linked to ring compounds, the rings being either naphthenic or aromatic in character. As far as is known, olefins and diolefins are not found in the original crude. Analyses of various types of crude oils show that they contain on the average two atoms of hydrogen, or slightly less per atom of carbon. Actually, the ratio of hydrogen to carbon is higher in the lighter fractions (as exemplified by the lower paraffins: C_nH_{2n+2}), but decreases gradually as the molecular weight rises. The hydrogen content of the high-boiling

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fractions therefore is considerably lower than the average 2:1 ratio. This progressive decrease in the hydrogen-carbon ratio with increasing boiling point is an important factor in the cracking and hydrogenation of petroleum."

The literature on pyrolysis of hydrocarbons deals mainly with lower temperatures and longer contact times than are met in water gas practice. It is clear, however, that the aromatic hydrocarbons are the most stable toward heat and that when they do decompose they give off hydrogen rather than hydrocarbons of low molecular weight and that paraffines yield the largest proportion of fixed hydrocarbon gases. There would thus seem to be at least a fair ground for believing that the hydrogen content of a gas oil should give an indication of its carburetting value. The small value of tars as a carburetting agent might also be explained by their low percentage of available hydrogen; available hydrogen being defined as the surplus hydrogen after all of the oxygen in the compound has been calculated as in combination as H_2O .

One of the obstacles to the investigation of this relationship of available hydrogen to carburetting value has been the tediousness of the methods for ultimate analysis of a fuel. These methods have been shortened as described in another paper presented at this meeting⁹ whereby a complete analysis for carbon, hydrogen, oxygen, nitrogen and sulphur can be completed in connection with a determination of heating value in a bomb calorimeter in less than four hours. Another of the obstacles to an investigation of this relationship has been removed with the improvement of laboratory cracking furnaces and the improved adaptability of the modern water gas set to carburetting oils of various types.

It seemed therefore worth while to secure samples of gas oils whose carburetting values had already been determined in a laboratory cracking unit and if possible confirmed by plant tests, and to make ultimate analyses of these oils and determine if there was any correlation to be found between the available hydrogen content and the carburetting value as determined experimentally.

Experimental Data on Gas Oils

The first group of samples was obtained through the courtesy of A. Holmes of the Standard Oil Company of New Jersey and were some of the oils used in the study to which reference has been made.⁴ Eight samples of oil submitted by Holmes were analyzed and the percentages of hydrogen compared with his experimental data on carburetting value. The data are given in Table I and the relationship of the hydrogen percentage to the carburetting value expressed as pounds of oil for 1,000 cu.ft. of 530 B.t.u. gas is shown in Figure 1.

Additional samples of gas oils of known carburetting value were then secured from the Detroit City Gas Company, the Consolidated Gas Co. of New York and the Marysville Plant of the Detroit Edison Company. These samples were all analyzed for hydrogen and the data, together with the information furnished by the donors of the samples, are to be found in Table I. The values furnished by the Detroit City Gas Company were determined in their cracking furnace at 1400, 1500 and 1600° F. There was no great variation between the three temperatures, and the data for 1500° are used in this paper. The data from the Consolidated Gas Company were obtained in their laboratory cracking furnace.⁶ The values reported are those taken from the curves at 1500° F. and the volume of oil gas has been taken as 50 cu.ft. per gallon. These figures represent substantially the optimum conditions for all except the heavy oil 130-32 and correspond to the conditions under which the other oils were tested. With this heavy oil optimum conditions were obtained in the cracking furnace at 1600° F. with 45 cu.ft. of oil gas per gallon and 75,000 B.t.u. per gallon of oil. Under these more favorable conditions 34.0 pounds of oil would be needed for each thousand cu.ft. of 530 B.t.u. gas instead of 36.7 as reported in Table I.

The data from the Marysville plant of the Detroit Edison Company came from the plant tests made by E. S. Pettyjohn in his research work for the Michigan Gas Association. These tests were made with bituminous coal as a generator fuel.

Before discussing the results it should perhaps be reiterated that the only work which we have done has been to make the ultimate analyses of the oils and to recalculate the results of the carburetting values to a uniform basis of pounds of oil per thousand cu.ft. of 530 B.t.u. gas. The heating value of blue gas from a coke generator has been taken as 290 B.t.u. per cu.ft.

Table I contains data on 35 oils varying from a light gas oil with a specific gravity of 0.8163 and a hydrogen content of 14.17% to a heavy residuum with a specific gravity of 1.0377 and a hydrogen content of 9.14%. The interpretation of the data can best be obtained from Figure 1 which correlates the carburetting value with the percentage of hydrogen. Curve A includes the results from all of the oils furnished by the Standard Oil Company of New Jersey, the Consolidated Gas Company and the Detroit City Gas Company. One of the points is far off of the curve and there is no explanation to be offered for the discrepancy. The carburetting test was made some months before we asked for the sample for ultimate analysis and only a small laboratory sample of the oil had been saved so that it was not possible to repeat the furnace test. The other 18 samples all fall fairly close to the

TABLE I
Data on Gas Oils

Oil Number	Sp.G. 60°/60°	Source and Type	A.S.T.M. IBP. 20%	Distillation		Carbureting		Chemical Analysis				Total		
				50%	75%	B.t.u./ Gal.	M Gals./ M	Cu.Ft.	Cu.Ft.	% H	% S		% N	% Ash
Std. Oil Co. of N. J. Samples														
BYV	0.8525		350			94.0	2.94	20.92	87.79	11.15	1.02	0.07	0.02	100.05
COL-OO	0.8763					93.3	2.85	20.84	87.13	11.20	1.58	0.14	0.02	100.07
WT-CS	0.9024	Cracked Gas Oil West Texas	350	561	760	84.1	3.33	25.02	89.12	10.46	0.30	0.17	0.03	100.08
WT-CS-FB	0.8866	Cracked Gas Oil	473	517	578	88.2	3.27	24.12	86.50	10.55	1.27	0.59	0.04	98.95
PA-OO	0.8163		345	543	702	118.5	2.38	16.17	85.80	14.17	0.02	0.03	0.00	100.02
WT-OO-SE	0.9001		385	575	740	88.6	3.34	25.10	85.37	12.89	1.64	0.09	0.02	100.01
PGOB-30	0.9001	Paraffin Gas Oil	296	720	777	97.6	2.85	21.36	87.00	12.10	0.75	0.07	0.00	99.92
WT-CS-FC	0.9106		542	588	690	59.5	5.10	38.67	86.37	9.68	1.41	0.19	0.03	97.67
Detroit City Gas Co. Samples														
6438	0.9908	Dubbs Residue				89.0	3.22	26.80	89.33	10.00	0.99	0.04	0.00	100.36
344	0.9609	Bunker C Oil	410	599	715	101.5	2.75	22.05	86.50	11.40	1.91	0.07	0.09	99.97
2221	0.9216	Low Viscosity Fuel Oil	432	501	567	82.4	3.53	27.13	88.65	10.10	0.57	0.41	0.00	99.73
6742	0.9032	Refinery Cracking Stock	397	608	704	104.3	2.67	20.12	87.43	12.25	0.49	0.13	0.00	100.30
1962	0.8800	Topped Michigan Crude	441	538	686	103.7	2.69	19.70	86.98	12.52	0.88	0.16	0.00	100.54
1136	0.8594	Motor Oil Diluents	322	397	770	96.2	2.94	21.02	87.55	11.90	0.10	0.28	0.08	99.91
6721	0.8240	Straight Run Gas Oil	418	516	629	113.8	2.41	16.60	86.68	13.25	0.00	0.12	0.00	100.05
Consolidated Gas Co. Samples														
362-33	0.8537	Straight Run	375	495	618	117.0	2.34	16.65	86.27	13.00	0.38	0.16	0.00	99.81
363-33	0.8573	Straight Run	340	529	657	120.0	2.27	16.23	85.98	13.18	0.36	0.31	0.00	99.63
366-33	0.9352	Straight Reduced Crude				107.0	2.59	20.20	86.07	11.76	1.69	0.17	0.03	99.80
130-32	1.0377	Pressure Still Residium				71.0	4.24	36.71	87.54	9.14	2.51	0.53	0.01	99.72
Marysville Samples														
M-4	0.8390					2.76	19.28	88.46	10.80	0.06				
M-6	0.8393					2.23	15.59	87.78	12.30	0.00				
M-9	0.8600					2.62	18.75	87.70	11.05	0.24				
M-12	0.8433					2.43	17.03	85.12	12.03	0.86				
M-14	0.8433					2.55	17.89	87.67	11.25	0.41				
M-15	0.8426					2.50	17.51	88.20	11.71	0.12				
M-17	0.8550					2.58	18.37	87.11	11.42	0.34				
M-19	0.8334					2.61	18.32	87.50	11.20	0.41				
M-5	0.8396					2.45	17.13	88.14	11.72	0.11				
M-7	0.8375					2.67	18.62	88.64	10.92	0.37				
M-10	0.8604					2.67	19.16	89.12	10.45	0.27				
M-11	0.8600					2.69	19.28	89.47	10.46	0.11				
M-13	0.8460					2.45	17.26	88.03	11.60	0.67				
M-16	0.8397					2.76	19.28	88.41	10.41	1.00				
M-18	0.8540					2.79	19.82	88.87	10.43	0.51				
M-20	0.8435					2.68	18.79	88.71	10.92	0.12				

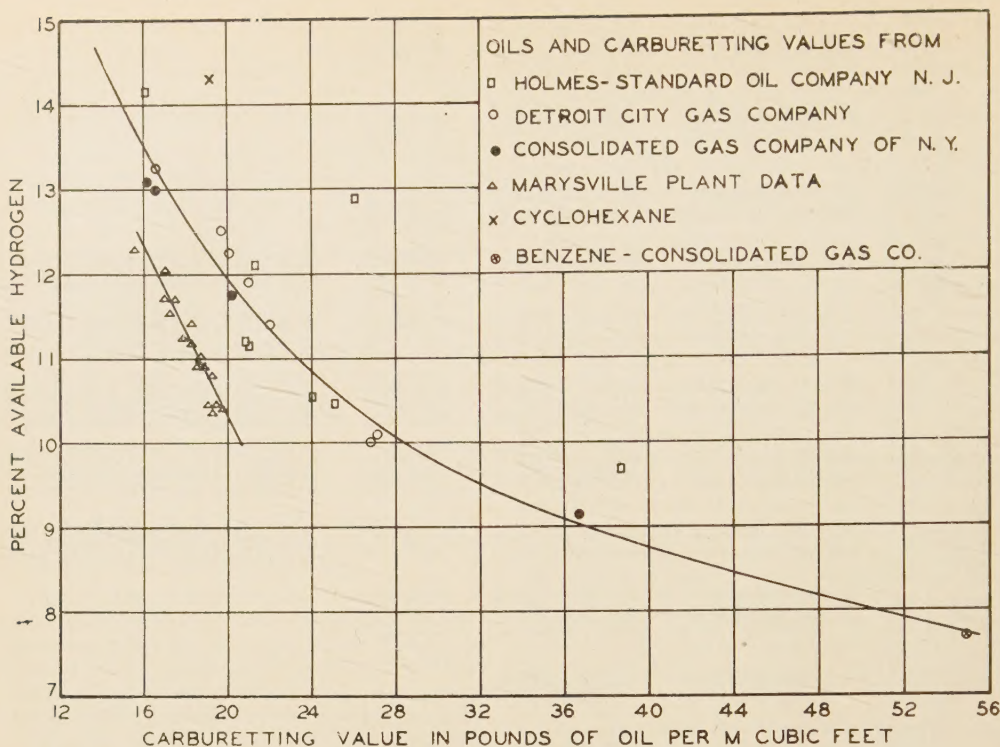


Figure 1. Relation of Available Hydrogen Content and Carburetting Value

curve, perhaps unexpectedly close when the variety of oils and the diversity of furnace tests is considered.

Carburetting tests on two pure compounds are also included in Figure 1. The value for cyclo-hexane is taken from the report of Murphy.⁷ His apparatus and procedure were somewhat different from those used by the other investigators but the result is in general agreement with the others. The test showing that 54.9 pounds benzene (C_6H_6) with 7.7% H were needed per 1,000 feet of 530 B.t.u. gas, was made at the laboratory of the Consolidated Gas Company of New York in order to determine how a cyclic compound with low hydrogen would behave. The result falls on a prolongation of the curve which passes through the other points.

The results of Pettyjohn from full plant scale tests fall on a straight line which is steeper than the curve obtained from the laboratory cracking tests. It should be repeated, however, that these results of Pettyjohn were obtained with a producer using bituminous coal as fuel and therefore the quantity of oil required to produce 530 B.t.u. gas should be less than when coke is used as fuel. The curves support this assumption.

Carburetting Value of Tar and Alcohol

The carburetting value of tar has been a disputed question, but the general impression has

been that it was valueless as a carburetting agent. Two samples of coal tar and two of water gas tar from the works of the Grand Rapids Gas Company were analyzed with results to be found in Table II. It will be observed that the percentage of hydrogen varies from 4.90 to 5.10, far below the lowest value of the petroleum oils tested.

Ultimate analyses of low temperature tars have been reported by Davis and Galloway⁸ and their data are also reported in Table II. The total hydrogen values range from 7.2 to 9.0 but the available hydrogen remaining after deducting for the oxygen of the tars varies from 6.2 to 8.4, a value which is lower than that of any of the gas oils reported. The figures on available hydrogen content thus confirm the opinion that tars have very little carburetting value.

In order to provide a test on another compound with considerable oxygen, the Consolidated Gas Company determined the carburetting value of absolute ethyl alcohol in their experimental cracking unit. C_2H_5OH contains 13.05% total and 8.7% available hydrogen. It should therefore have a higher carburetting value than benzene with 7.7% hydrogen. The alcohol does yield 82.0 M B.t.u. per gallon as compared with 39.0 M B.t.u. per gallon of benzene. However, the gas formed from alcohol has a heating value of only 498 B.t.u. per cu.ft. and so it manifestly is

TABLE II
Data on Tars

Kind of Tar	Sp. G.	% C	% H	Chemical Analysis		% Available Hydrogen
				% S	% O	
Coal Tar		92.00	5.10	2.00		
		91.82	5.00	1.80		
Water Gas Tar		93.16	5.40	0.38		
		91.75	4.90	1.85		
Low Temperature Tar ^s	1.0687	85.5	8.2	0.7	4.8	7.6
	1.0622	84.3	8.4	0.7	5.9	7.7
	1.0888	87.0	7.2	0.9	4.4	6.7
	1.0556	78.5	8.5	1.1	11.3	7.1
	1.0945	82.1	7.3	0.5	9.2	6.2
	1.0204	83.4	9.0	0.9	6.2	8.2

impossible to use alcohol to enrich 290 B.t.u. blue gas to a value of 530 B.t.u. The detrimental effect of oxygen is thus greater than would be accounted for on the basis of its available hydrogen. This confirms the opinion that tars can have very little carburetting value.

Conclusions

The percentage of available hydrogen in a gas oil has been shown to bear a close relation to its carburetting value. Results are presented for three groups of gas oils which had been tested in the laboratory cracking units of the three companies furnishing them. These carburetting values are correlated with the percentage of hydrogen and the results for the 19 oils varying in specific gravity from 0.8163 to 1.0377 fall, with one exception, fairly well on a curve whose trend is indicated by the following numerical values:

Per Cent of Available Hydrogen in Oil	Pounds of Oil Required for 1000 Cu.Ft. of 530 B.t.u. Gas
14.0	14.0
12.0	19.6
10.0	28.0
9.0	37.0
8.0	51.0

These data indicate that gas oil with 14.0% hydrogen is worth twice as much per pound as one with 10.0% hydrogen and that the carburetting value of oils falls off very rapidly when the hydrogen is below 9%. Since modern coal and water gas tars contain only about 5%, and low temperature tars only 6 to 8% of hydrogen it appears that their carburetting value will be negligible.

When bituminous coal is used as generator fuel instead of coke, less oil is required to produce a gas of desired heating value. Results of plant tests of 16 oils show a good correlation with the hydrogen content and the curve does show a smaller amount of oil is required. The slope of the curve indicates that heavy oils may be used more advantageously with bituminous coals than with coke, but the data are not complete enough to do more than make this as a suggestion, which has some theoretical as well as experimental justification.

This correlation of available hydrogen content with the carburetting value of gas oils seems to hold with a wide variety of oils and to deserve a more careful study.

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